

IAP20 Rec'd PCT/EP 29 MAR 2006

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IONIC LIQUIDS AS SUPPORTS.

- 5 The present invention relates to the use of ionic liquids to prepare supported catalyst components for olefin polymerisation.

Ionic liquids have been described in literature such as for example in US -A- 5,994,602, or in WO96/18459 or in WO01/81353. They disclose various methods  
10 for preparing ionic liquids and various applications.

These applications comprise oligomerisation of ethene, propene or butene with various nickel-based precursors dissolved in ionic liquids as disclosed for example in Dupont et al. (Dupont, J., de Souza R.F., Suarez P.A.Z., in Chem.  
15 Rev., 102, 3667, 2002.). The same document also discloses that Ziegler -Natta type polymerisation can be carried out in dialkylimidazolium halides/ammonium halide ionic liquids using  $AlCl_{3-x}R_x$  as cocatalysts.

Other applications include the use of ionic liquids that are liquid at or below room  
20 temperature as solvents for transition -metal-mediated catalysis, such as described for example in Welton (Welton T., in Chem . Rev., 99, 2071, 1999.). Most attempts have proven successful in dimerisation or oligomerisation, but polymerisation remains problematic, especially with single site catalyst components.

25 There is thus a need to develop new single site catalyst systems based on ionic liquids that are active in the polymerisation of alpha -olefins.

It is an aim of the present invention to provide a method for preparing a single  
30 site catalyst component supported on an ionic liquid.

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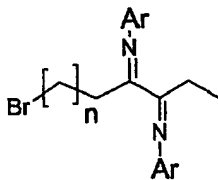
It is another aim of the present invention to provide a single site catalyst component supported on an ionic liquid.

It is a further aim of the present invention to provide a process for polymerising  
5 alpha-olefins using such supported single site catalyst component.

It is also an aim of the present invention to prepare new polymers with said new catalyst system.

10 Accordingly, the present invention discloses a method for preparing a supported single site catalyst component for the polymerisation of alpha-olefins that comprises the steps of:

a) providing a halogenated bisimine precursor component of formula (I)

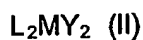


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(I)

b) reacting the halogenated bisimine precursor with an ionic liquid precursor in a solvent to prepare an ionic liquid;

c) reacting the ionic liquid obtained in step b) with a metallic precursor of  
20 formula (II) in a solvent



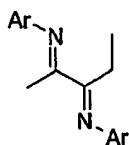
wherein L is a labile ligand, M is a metal selected from Ni or Pd and Y is a halogen;

d) retrieving a supported single site catalyst component.

25

The halogenated bisimine precursor is obtained by reacting

- a bisimine of formula III

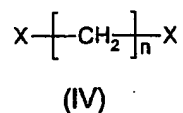


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(III)

wherein each Ar can be the same or different and is a substituted or unsubstituted benzene ring Bz-R, wherein R is hydrogen or an alkyl having from  
 10 1 to 12 carbon atoms. The benzene ring is preferably substituted in positions 2 and 6, and the preferred substituents are methyl, ethyl, isopropyl

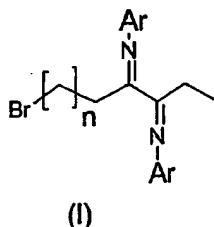
- with lithium diisopropylamide or lithium tert-butyrate at a temperature of from – 78 to –10 °C , preferably at a temperature of about –30 °C and for a period of  
 15 time of from 30 minutes to 3 hours and preferably of from 30 minutes to 1 hour;  
 - and then with a compound of formula IV



wherein X is a halogen and n is an integer of from 2 to 12, preferably from 5 to 8  
 20 and more preferably equal to 6, at a temperature of from – 78 to –10 °C up, and then slowly returning to room temperature (about 25 °C) for a period of time of from 30 minutes to 16 hours, preferably of about one hour.

All reactions are carried under argon at atmospheric pressure, using the standard  
 25 Schlenk or glovebox techniques.

The resulting halogenated bisimine is represented by formula I.



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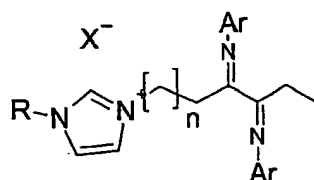
The halogenated bisimine is then reacted with an ionic liquid precursor, preferably N-alkylimidazole or pyridine, in a solvent such as tetrahydrofuran (THF),  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  or without solvent.

- 10 In the ionic liquid, the anion  $\text{X}^-$  can be selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . It can also be selected from compounds of formula  $\text{AlR}_{4-z}\text{X}^z$  wherein R can be selected from an alkyl having from 1 to 12 carbon atoms, substituted or unsubstituted, or from a cycloalkyl having 5 or 6 carbon atoms, substituted or unsubstituted, or from an heteroalkyl, substituted or
- 15 unsubstituted, or from an heterocycloalkyl, substituted or unsubstituted, or from an aryl having 5 or 6 carbon atoms, substituted or unsubstituted, or from an heteroaryl, substituted or unsubstituted, or from an alkoxy, an aryloxy, an acyl, a silyl, a boryl, a phosphino, an amino, a thio or a seleno, wherein  $\text{X}^z$  is a halogen and wherein z is an integer from 0 to 4. The cationic part of the ionic liquid may
- 20 be prepared by protonation or alkylation of a compound selected from imidazolium, pyrazoline, thiazole, triazole, pyrrole, indone, tetrazole, pyridine, pyrimidine, pyrazine, pyridazine, piperazine or piperidine.

- Preferably, the anion  $\text{X}^-$  is  $\text{Br}^-$  or  $\text{BF}_4^-$ , and preferably the cationic part is derived
- 25 from imidazolium or pyridinium, and the ionic liquid precursor is thus preferably N-alkylimidazole or pyridine.

If the ionic liquid precursor is N-alkyl-imidazolium, the reaction is carried out at a temperature of from 50 to 80 °C, preferably of from 60 to 70 °C and for a period of time of from 1 to 24 hours, preferably of from 4 to 6 hours. The resulting

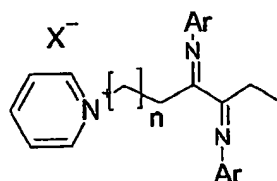
5 intermediate product is an ion pair of formula V.



(V)

10 If the ionic liquid precursor is pyridinium, the reaction is carried out at a temperature of from 20 to 80 °C, preferably of from 50 to 70 °C and for a period of time of from 1 to 5 days, preferably of about 3 days. The resulting product is an ion pair of formula VI

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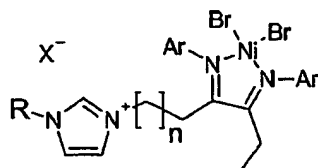


(VI)

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The intermediate product V or VI is then reacted with a metallic complex of formula L<sub>2</sub>MY<sub>2</sub> in a solvent selected typically from CH<sub>2</sub>Cl<sub>2</sub>, THF, or CH<sub>3</sub>CN, at room temperature (about 25 °C), for a period of time of from 1 to 24 hours,

preferably of from 14 to 18 hours. The resulting product is an ion pair representing a supported catalytic component of formula VIII if the ionic liquid is a N-alkyl-imidazolium

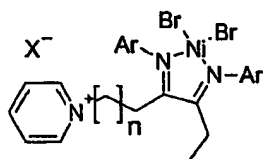


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(VII)

or of formula VIII if the ionic liquid is pyridinium

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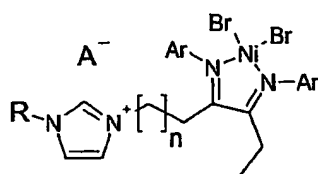
(VIII)

15 wherein M, Ar and Y are as defined here -above.

Optionally, before the reaction with the metallic complex is carried out, the intermediate product (VI) or (VII) can be reacted with a salt  $C^+A^-$ , wherein  $C^+$  is a cation that can be selected from  $K^+$ ,  $Na^+$ ,  $NH_4^+$ , and  $A^-$  is an anion that can be selected from  $PF_6^-$ ,  $SbF_6^-$ ,  $BF_4^-$ ,  $(CF_3-SO_2)_2N^-$ ,  $ClO_4^-$ ,  $CF_3SO_3^-$ ,  $NO_3^-$  or  $CF_3CO_2^-$ .  
 20 The reaction is carried out in a solvent selected typically from  $CH_2Cl_2$ , THF or  $CH_3CN$  at a temperature of from 50 to 80 °C, preferably of about 60 °C and for a period of time of from 6 to 48 hours, preferably of from 16 to 24 hours.

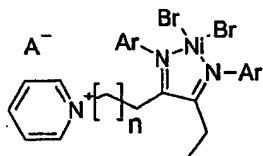
The reaction with the metallic complex is then carried out as previously leading to an ion pair representing a supported catalytic component of formula IX if the ionic liquid precursor is N-alkyl-imidazolium

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(IX)

10 or of formula X if the ionic liquid precursor is pyridinium



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(X)

The present invention also discloses a catalytic component supported on an ionic liquid, obtainable by the method described here -above.

20 An active supported catalyst system is then obtained by addition of an activating agent.

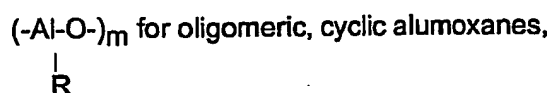
The activating agent can be selected from alumoxanes or aluminium alkyls or boron-based activating agents.

The aluminium alkyls are of the formula  $\text{AlR}_x$  and can be used wherein each R is  
 5 the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminium alkyls are dialkylaluminum chloride, the most preferred being diethylaluminum chloride ( $\text{Et}_2\text{AlCl}$ ).

10 The preferred alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :



15 and



20

wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a  $\text{C}_1$ - $\text{C}_8$  alkyl group and preferably methyl.

Methylalumoxane (MAO) is preferably used.

25 Suitable boron-based activating agents may comprise triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium  $[\text{C}(\text{Ph})_3^+ \text{B}(\text{C}_6\text{F}_5)_4^-]$  as described in EP-A-0,427,696

Other suitable boron-containing activating agents are described in EP-A-0,277,004.

30

The amount of activating agent is such that the Al/M ratio is of from 100 to 1000.



The present invention further provides a method for homopolymerising or for copolymerising alpha-olefins that comprises the steps of:

- 5 a) injecting the catalytic component supported on an ionic liquid, an apolar solvent and the activating agent into the reactor;
- b) injecting the monomer and optional comonomer into the reactor;
- c) maintaining under polymerisation conditions;
- d) retrieving the polymer under the form of chips or blocks.

- 10 The conditions of temperature and pressure for the polymerisation process are not particularly limited.

The pressure in the reactor can vary from 0.5 to 50 bars, preferably from 1 to 20 bars and most preferably from 4 to 10 bars.

15

The polymerisation temperature can range from 10 to 100 °C, preferably from 20 to 50 °C and most preferably at room temperature (about 25 °C).

- 20 The solvent is apolar and is typically selected from an alkane, preferably n - heptane.

The reaction is carried out for a period of time of from 30 minutes to 24 hours.

- 25 The polymer obtained according to the present invention is typically obtained as a mixture of chips and blocks, wherein the amount of blocks is predominant. The chips have a size of from 0.5 to 5 mm and the blocks have a size of from 5 mm to 5 cm, preferably of about 1 cm. The amount of chips is typically less than 25 wt%, based on the total weight of the polymer, preferably less than 15 wt%.

- 30 The monomer that can be used in the present invention are alpha-olefins having from 3 to 8 carbon atoms and ethylene, preferably ethylene and propylene.

**List of figures.**

Figure 1 represents the ethylene consumption expressed in mL as a function of time expressed in minutes for catalyst systems based on imidazolium and respectively on  $\text{BF}_4^-$  or on  $\text{Br}^-$  counter-anion.

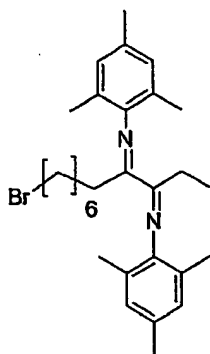
Figure 2 represents the ethylene consumption expressed in mL as a function of time expressed in minutes for catalyst systems based respectively on pyridinium and imidazolium.

**Examples.**

All reactions were carried out on a vacuum line under argon using standard glovebox and Schlenk techniques.

**Synthesis of supported catalyst components using different ionic liquids.**

**Synthesis of halogenated bisimlne (1).**



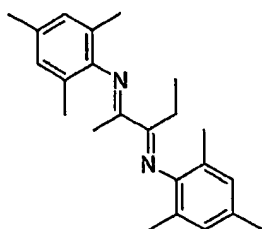
For preparing a preliminary solution of lithium diisopropyl amide (LDA) 0.41 mL of butyllithium (1.6 molar in hexane) were added to 0.101 mL (0.72 mmoles) of isopropylamine in THF at a temperature of  $-35^{\circ}\text{C}$ . In a Shlenk tube under argon, 155 mg (0.46 mmoles) of bisimine were introduced in 5 mL of THF and then cooled to a temperature of  $-35^{\circ}\text{C}$ . The solution of LDA was then added dropwise at a temperature of  $-35^{\circ}\text{C}$  and stirred for 30 minutes until the reaction mixture turned red. That solution was syringed into a solution of 0.184 mL (1.19 mmoles) of 1,6-dibromohexane that was cooled to a temperature of  $-35^{\circ}\text{C}$  and the resulting mixture was stirred for 1 hour at a temperature of  $-35^{\circ}\text{C}$  and then for 16 hours at room temperature. The THF was evaporated and 5 mL were added to form a white precipitate. It was filtered and the filtrate was concentrated into yellow oil. A column on silica gel with a gradient of pentane to pentane/toluene (80/20) as eluent was carried out to retrieve 220 mg of yellow oil with a yield of 95 %.

$^1\text{H}$  and  $^{13}\text{C}$  NMR carried out on the product gave the following results:

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.88 (s, 4), 3.33 (tr, 2), 2.53 (q, 2), 2.49 (tr, 2), 2.28 (s, 6), 2.01 (s, 12), 1.76 (q, 2), 1.47 (m, 2), 1.25 (m, 6), 1.02 (tr, 3).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$ : 172.22, 171.07, 145.82, 132.25, 128.66, 124.62, 33.81, 32.72, 29.71, 29.06, 28.23, 27.66, 26.41, 22.34, 20.71, 18.17, 11.20.

#### Synthesis of bisimine (3).



In a solution of 40 mL of dichloromethane, 0.628 mL (6 mmoles) of 2-5  
pentanedione and 5.86 mL (42 mmoles) of 2,4,6 trimethylaniline were added and  
cooled down to a temperature of  $-20^{\circ}\text{C}$ . A solution of 0.59 mL (7.1 mmoles) of  
 $\text{TiCl}_4$  was added dropwise at a temperature of  $-20^{\circ}\text{C}$  and then stirred for 30  
5 minutes at  $-20^{\circ}\text{C}$ , until the reaction mixture turned red. The mixture was brought  
back to room temperature and stirred for 5 days. The dichloromethane was  
evaporated and 120 mL of diethyl ether were added to form a precipitate. After  
filtering, the filtrate was concentrated into a brown solid that was washed with 20  
mL of methanol in order to retrieve 1.575 g of yellow powder with a yield of 78.5 %.

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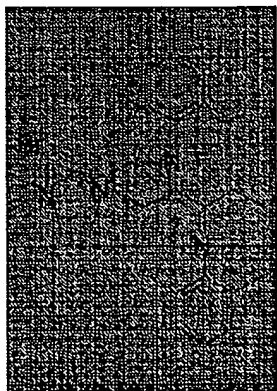
$^1\text{H}$  and  $^{13}\text{C}$  NMR carried out on the product gave the following results:

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.86 (s, 4), 2.50 (q, 2), 2.26 (s, 6), 1.99 (s, 15),  
1.00 (tr, 3).

15

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$ : 172.73, 145.67, 132.41, 128.64, 124.55, 22.21,  
20.77, 17.95, 16.36, 11.44.

Ion pair (5).



20

In a Schlenk tube under argon, 5 mL of THF were introduced followed by 100 mg (0.201 mmoles) of the halogenated bisimine (I). 0.032 mL (0.402 mmoles) of N-methylimidazole were then added. The reaction medium was refluxed at 66 °C for 5 hours and then at room temperature for 16 hours. It was then concentrated under vacuum to produce yellow oil that was washed three times with 3 mL of diethyl ether to yield a powder. That powder was dissolved in 1 mL of dichloromethane and then precipitated in 25 mL of pentane. The precipitate was filtered then evaporated under vacuum to prepare 107 mg of yellow powder with a yield of 95 %.

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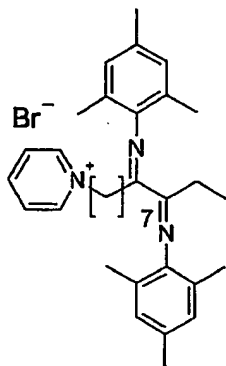
$^1\text{H}$  and  $^{13}\text{C}$  NMR carried out on the product gave the following results:

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.56 (s, 1), 7.22 (tr, 1), 7.10 (tr, 1), 6.68 (s, 4), 4.20 (tr, 2), 4.08 (s, 3), 2.51 (q, 2), 2.47 (tr, 2), 2.39 (s, 6), 1.99 (s, 12), 1.80 (m, 2), 1.43 (m, 2), 1.20 (m, 6), 1.00 (tr, 3).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$ : 172.7, 171.2, 146.11, 132.73, 129.11, 124.96, 123.47, 121.85, 55.79, 37.2, 30.66, 29.95, 29.42, 28.75, 26.71, 26.39, 22.77, 21.19, 18.60, 11.68.

20

Ion pair (6).



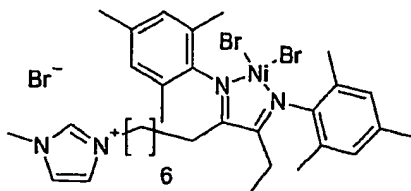
In a Schlenk tube under argon 45 mg (0.09 mmoles) of the halogenated bisimine (1) were added followed by 2 mL of pyridine as solvent. The solution was stirred at 90 °C for 15 hours. The pyridine was then evaporated and the residue was washed 3 times with 5 mL of diethyl ether. It was dissolved in 1 mL of dichloromethane, and then precipitated with 20 mL of pentane. The precipitate was filtered and dried to produce 24 mg of yellow powder with a yield of 45 %.

<sup>1</sup>H NMR carried out on the product gave the following results :

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ: 9.37 (d, 2), 8.43 (tr, 1), 8.03 (tr, 2), 6.85 (s, 4), 4.86 (tr, 2), 2.48 (q, 2), 2.40 (tr, 2), 2.24 (s, 6), 1.96 (s, 12), 1.90 (m, 2), 1.38 (m, 2), 1.18 (m, 8), 0.85 (tr, 3).

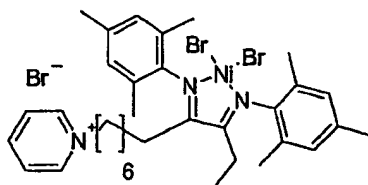
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**Synthesis of catalyst (7).**



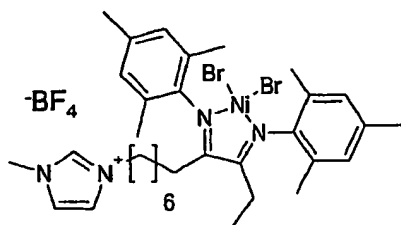
In a Schlenk tube under argon, 15 mL of dichloromethane were introduced followed  
 5 by 30 mg (0.052 mmoles) of the ion pair (5). 14.3 mg (0.046 mmoles) of  
 (DME)NiBr<sub>2</sub> were then added and the mixture was stirred during 16 hours at room  
 temperature until it turned orange. The dichloromethane was evaporated to produce  
 a brown oil. The oil is dissolved in 1 mL of dichloromethane and then precipitated  
 with 7 mL of pentane. The precipitate was filtered and dried to produce 31 mg of  
 10 brown powder with a yield of 75 %.

#### Synthesis of catalyst (8).



20 mg (0.035 mmoles) of the ion pair (6) were introduced under argon and 2 mL of  
 15 dichloromethane were then added. This was followed by the addition of 12.84 mg  
 (0.0416 mmoles) of (DME)NiBr<sub>2</sub> and the mixture was stirred for 16 hours at room  
 temperature. The solvent was evaporated and the residue was washed with 5 mL  
 of diethylether. It was then dissolved in 5 mL of acetone to form a precipitate. The  
 precipitate was filtered and dried to produce 14 mg of orange powder with a yield of  
 20 51 %.

#### Synthesis of catalyst (9).



In a Schlenk tube under argon, 45 mg (0.068 mmoles) of bisimine -imidazolium (BF<sub>4</sub><sup>-</sup>) were introduced followed by 5 mL of dichloromethane. 25.25 mg (0.081 mmoles) of (DME)NiBr<sub>2</sub> were then added and the mixture was stirred for 16 hours at room temperature. The solvent was evaporated and the residue was washed twice with 20 mL of diethylether. It was then dissolved in 5 mL of acetone to form a precipitate. The precipitate was filtered and dried to produce 50 mg of red powder with a yield of 91 %.

#### Polymerisation of ethylene.

The polymerisation conditions were the same for all for all examples and they were as follows:

- 5 μmoles of catalyst component were dissolved in 60 ml of n -heptane;
- 300 mole-equivalents of methylaluminoxane (MAO) were added;
- T= 25 °C;
- p= 4 bars,
- t=2 hours
- the polymer is treated with acid methanol (10 vol% HCl).

The polymerisation results are displayed in Table I.



TABLE I.

Catalyst	mass PE mg	Tf °C	Activity kgPE/mol/hr	Nature PE	% chips
7	4144	131.2	476	blocks/chips	14
9	8207	129.5	1266	blocks/chips	26
8	10442	129.4	1642	blocks/chips	9

5

The use of ionic liquids as support allows the preparation of precipitates that are easy to inject into the reactor.

- 10 As can be seen in Table I, the polymers are mostly obtained under the shape of blocks that are much safer and easier to handle than small size polymeric particles. It has also been observed that the fusion temperature of the polyethylene is comparable to that obtained with other catalyst systems, as well as the molecular weight and the polydispersity.

15

- The nature of the counter-anion has a significant influence on the activity of the catalyst system as can be seen in Figure 1 representing the consumption of ethylene expressed in ml as a function of time expressed in minutes respectively for Br<sup>-</sup> and for BF<sub>4</sub><sup>-</sup>. The catalyst system based on the BF<sub>4</sub><sup>-</sup> counter-anion has a much larger consumption of ethylene and thus a much larger activity than that based on the Br<sup>-</sup> counter-anion.
- 20

- The nature of the cation also plays a significant role in the activity of the catalyst system as can be seen in Figure 2 representing the consumption of ethylene expressed in mL as a function of time expressed in minutes respectively for pyridinium- and imidazolium-based ionic liquids. The catalyst system based on the pyridinium-type ionic liquid has a much larger consumption of ethylene and thus a much larger activity than that based on the imidazolium-type ionic liquid.
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